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Project Summary

Evaluation of the Resistance of a Chlorinated Polyethylene Protective Garment Material to Permeation and Degradation by Liquid Chemicals

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The objectives of this project were to investigate existing permeation and degradation resistance data for chlorinated polyethylene (CPE); to develop a laboratory test plan consistent with American Society for Testing and Materials (ASTM) Standard Test Methods F739-81 and D471-79 regarding permeation, solubility, swelling, and degradation of CPE fabric by test chemicals; and to obtain laboratory test data for chemical and CPE combinations of interest for which only limited or questionable permeation and degradation resistance data exist. Ten liquid chemicals (acetic acid, acetic anhydride, acetone, bis(2-chloroethyl)ether, carbon tetrachloride, ethylene diamine, isopropyl alcohol, N-nitrosodimethylamine, phenol, and o-xylene) were tested to determine permeation rates, breakthrough times, and swelling when contacted with 20 mil thick CPE. Mean permeation breakthrough times ranged from 15 minutes to over 8 hours. Steady-state permeation rates ranged from 0 to 170 mg • m^{-2} • sec^{-1}. Solubility and swelling data also showed wide variation depending upon the chemical. Soaking the CPE in one chemical resulted in a loss of weight, while contact with four other compounds resulted in weight gains by the CPE test swatch of over 100%. Chemical contact was also shown in 8 of 10 cases to reduce the capacity of the CPE for resisting tearing due to deformation.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Project Objectives/Approach/ Organization

The objectives of this project were to evaluate the permeation and degradation resistance of a 20 mil chlorinated polyethylene (CPE) chemical protective outer garment material when contacted by hazardous and toxic substances to which chemical spill and uncontrolled hazardous waste site response personnel may be exposed. To reach this objective, JRB Associates identified and evaluated the existing permeation and degradation data base as of August 1983; proposed a prioritized list of untested substances; and developed a preliminary laboratory permeation/degradation resistance test plan, which was based primarily on ASTM Method D-471-79, "Standard Test Method for Rubber Property—Effects of Liquids" and ASTM F-739-81. "Standard Test Method for Resistance of Protective

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Clothing Materials to Permeation by Hazardous Liquid Chemicals"; and managed the execution of this test plan by Rocky Mountain Analytical Laboratories (RMAL). An external audit of the permeation testing was conducted by IT Corporation-EERU. As part of the external audit, duplicate samples were subjected to permeation testing by Radian Corporation.

Rationale for Evaluating the Performance of 20 mil CPE

The U.S. Environmental Protection Agency (EPA), pursuant to the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA), participates in response, investigation, mitigation, control, and cleanup of hazardous substance spills and uncontrolled hazardous waste sites. When conditions require it, EPA personnel utilize totally encapsulating ensembles to provide protection from dermal and respiratory contact with hazardous substances. Based on their field experiences with totally encapsulating ensembles, EPA personnel expressed a need in 1981 for an ensemble with a self-contained, long-term air supply; breathing air and body cooling; and total body protection from chemical splashes or vapors and from pinholes or leaking seals in the protective outer garment. The U.S. Army's Chemical Systems Laboratory (since re-named the Chemical Research and Development Center) and the U.S. Coast Guard had developed a prototype ensemble that potentially met EPA's requirements. The EPA entered into an Interagency Agreement with the U.S. Army in 1982 to advance the development of the prototype ensemble, named the Long-term, Self-contained, Chemical Protective Ensemble (LSCPE).

The current LSCPE outer garment consists primarily of 20 mil chlorinated polyethylene (CPE), which had previously been selected by the Army after extensive evaluation and testing for use in its Demilitarization Protective Ensemble. However, the outer garment only required that penetration testing be conducted with "(chemical warfare) agents, decontaminants, hydraulic fluids, and other liquid substances present in the toxic area and liable to come into contact with the ensemble."[1] For EPA's intended use of the LSCPE, additional data were required on the degradation and permeation resistance of CPE when in contact with chemical substances that EPA personnel were likely to encounter at chemical spills and uncontrolled hazardous waste sites.

Materials and Methods

CPE Test Samples and the Ten Challenge Chemicals

Test samples of CPE were provided by ILC Dover. The sample material was designated as 20 mil Cloropel™ alloyed CPE (ILC part number ST92C019-03, lot 2). All swatches were smooth, without seams.

The selection of the challenge chemicals to be tested was based primarily upon a literature search designed to identify the chemicals most commonly found in hazardous chemical spills and at hazardous waste disposal sites. The list of challenge chemicals selected originally numbered 50, and tests were performed on 10 of those compounds. The 10 chemicals used to test CPE were acetic acid, acetic anhydride, acetone, bis-(2-chloroethyl) ether, carbon tetrachloride, ethylenediamine, isopropanol, N-nitrosodimethylamine, phenol, and ortho-xylene.

Methodology for Determining Breakthrough Times and Permeation Rates

Breakthrough times and permeation rate measurements were performed with minor variations according to the American Society for Testing and Materials (ASTM) Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Hazardous Liquid Chemicals (F739-81). This method requires that the protective material be clamped into a test cell and then be subjected to chemical contact on one side and a collecting medium on the other side. The collecting medium is sampled over time to determine whether any of the test chemical has permeated the membrane. The principal data generated are the breakthrough time and the steady-state permeation rate of the chemical through the polymer membrane. Breakthrough time is the "elapsed time between initial contact of the hazardous liquid chemical with the outside surface of a protective clothing material and the time at which the chemical can be detected at the inside surface of the material by means of the chosen analytical technique." Steady-state permeation is "the constant rate of permeation that occurs after breakthrough when all forces affecting permeation have reached equilibrium."[2]

Methodology for Measuring the Solubility and Swelling of CPE Caused by Immersion in Liquid Test Chemicals

ASTM Standard Method D471-79 (Rubber Property—Effect of Liquids) was used to determine the solubility and swelling of the CPE material after immersion into the 10 test chemicals.

The general procedure used was as follows. Triplicate CPE swatches for each test chemical were cut into approximately 25 mm × 50 mm rectangles. The mass, length, width, and thickness of the swatches were then determined before immersion into the test chemical. After immersion into the test chemical, the swatches were removed at intervals of approximately 5 min, 15 min, 30 min, 60 min, 3 hours and 24 hours and the above measurements were performed again. The tests were continued until saturation was achieved or until a 24 hour immersion period had occurred. Saturation was defined as having been achieved if successive mass measurements differed by less than 2%.

The percent change in mass due to saturation or immersion in the test chemical for 24 hours was determined using the following formula:

$$\Delta M\ (\%) = (M_2 - M_1)/M_1 \times 100\%$$

where:

ΔM = percent mass change
M_1 = mass of the CPE swatch after saturation with the test chemical or immersion in the test chemical for 24 hours, whichever came first
M_2 = Initial mass of the CPE swatch prior to the first immersion in the test chemical

Analogous formulas were used to calculate the percent length, width and thickness changes due to chemical saturation.

Methodology for Measuring the Degradation of CPE Following Immersion In Liquid Chemicals

A non-standard test was performed to measure the degradation of chemical-soaked CPE when subjected to repeated physical deformation. Three CPE

[1]The Demilitarization Protective Ensemble, Volume I—The Development Program, An Overview. U.S. Army Chemical Systems Laboratory, 1982, p. 24.

[2]Definitions are from the ASTM Method F-739-81.

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Table 1. *Breakthrough Times of Test Chemicals Through 20 mil CPE*

Chemical	RMAL Breakthrough Time (min) Raw	RMAL Breakthrough Time (min) Mean	R.S.D %	Radian Breakthrough Time (min) Raw	Radian Breakthrough Time (min) Mean	R.S.D. %	RMAL and Radian Mean Breakthrough Time (min)	R.S.D. %
Acetic Acid	265 241 205	237	12.7	140 146 147	144	2.6	191	28.5
Acetic Anhydride	86 76 64	75	14.6	72 72 72	72	0	74	9.8
Acetone	16 18 18	17	6.7	15 15 15	15	0	16	9.1
Bis-(2 Chloroethyl) ether	99 56 61	72	32.7	91 83 87	87	4.6	80	21.6
Carbon Tetrachloride	245 199 183	209	15.4	205 210 207	207	1.2	208	9.8
Ethylenediamine	128 131 101	120	13.3	154 159 167	160	4.1	140	17.3
Isopropanol	N/A	<1	N/A	>480 >480 >480	>480	N/A	N/A	N/A
N-Nitrosodimethylamine	38 32 21	30	28.4	42 42 42	42	0	36	23.2
Phenol	184 224	204	13.5	165 180 180	175	5.0	187	11.8
O-Xylene	77 72 67	72	6.9	62 66 60	63	4.9	67	9.3

swatches per chemical were immersed into the liquid test chemicals using the same procedures as those described previously. Every swatch was then subjected to prodding to a depth of 0.5 inches by a blunt steel rod at a rate of 10 ± 2 times per minute. Every two hours, the swatch was inspected and observed for changes in color, surface smoothness or shape with respect to a control swatch which had not been saturated with the test chemical but had been subjected to the same repeated prodding.

The apparatus used to subject the CPE swatches to deformation consisted of an electrically driven motor connected to a series of belts and pulleys. The pulleys were chosen to produce the desired rate of prodding and to allow the blunt rod to prod the swatch to a depth of 0.5 inches (13 mm). After a swatch was saturated with the test chemical, it was held perpendicular to the prodding rod with a 1 inch brass union.

Results and Discussion

Breakthrough Times and Permeation Rates of Test Chemicals Through CPE

Breakthrough times and steady-state permeation rates for the 10 test chemicals passing through the CPE test swatches are listed in Tables 1 and 2. Mean breakthrough times from both laboratories are in relatively close agreement between 8 of the 10 pairs of data. There was a major difference between the mean breakthrough times for acetic acid (237 min vs. 144 min). No explanation for the discrepancy was found, but both mean breakthrough times represent significant resistance to permeation. There was also a major difference (<1 min vs. >480 min) between the individual laboratory mean breakthrough times for isopropanol. The low (<1 min) values were discarded in the evaluation of CPE performance, because (a) the resistance of CPE to another alcohol (methanol) was found from other data to be much greater than one minute, (b) CPE did not show signs of degradation as a result of contact with isopropanol, and (c) similar very short breakthrough times for carbon tetrachloride were generated and discarded, since good precision both within and between laboratories was demonstrated for high breakthrough times that were generated for the car-

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bon tetrachloride. It is assumed that the cause of the low breakthrough times for isopropanol are the same as for the carbon tetrachloride.

In the case of carbon tetrachloride, breakthrough times from one lab fell into two distinct groups, <1 minute and 183-245 minutes. The second laboratory's data were in the 205-210 minute range. The low breakthrough times were discarded due to the close agreement on the high values between two independent laboratories.

External Quality Assurance Program for Permeation Tests

An external quality assurance audit of the permeation testing was conducted. The purpose of the program was to ensure an acceptable degree of confidence in the data generated during the permeation testing of the 20 mil CPE outer garment material. This was accomplished through the use of performance evaluation samples, interlaboratory testing, and review of analytical protocols, internal quality control procedures, data, and analysis results.

Solubility and Swelling of Chlorinated Polyethylene Caused by Immersion In the Test Chemicals

Average percent increases in mass after saturation or immersion in the test chemical for 24 hours ranged from 0.5% for ethylenediamine to 126% for bis(2-chlorethyl ether). Test chemicals that caused percent mass increases of less than 100% of the original CPE swatch weight were ethylenediamine (0.5%), isopropanol (3.5%), acetic acid (29%), phenol (34%) and acetone (57.3%). Test chemicals that caused mass increases exceeding 100% of the original CPE swatch weight were carbon tetrachloride (100%), N-nitrosodimethylene (112%), o-xylene (112%) and bis(2-chloroethyl) ether (126%).

Performance of Chemical-Soaked CPE when Subjected to Repeated Physical Deformation

CPE swatches not exposed to any chemical formed shallow indentations but essentially recovered their initial shape after the test was terminated.

Chemicals that did not cause any of the triplicate trial swatches to tear during the two-hour deformation test period were acetic anhydride, carbon tetrachloride, and isopropanol. Chemicals that caused only one of the three test swatches to tear during the two hour deformation test were acetic acid, acetone and ethylenediamine. And chemicals that caused more than one of the three trial swatches to tear during the two hour deformation test were bis(2-chloroethyl) ether, N-nitrosodimethylamine, phenol, and o-xylene.

Table 2. Permeation Rates of Test Chemicals Through 20 mil CPE

Chemical	Permeation Rate ($mg \cdot m^{-2} \cdot sec^{-1}$) Raw	Mean	Radian R.S.D.
	10		65.7
Acetic Acid	10	7	
	2		
	10		
Acetic Anhydride	7	9	16.7
	9		
	169		
Acetone	146	170	14.1
	194		
	154		
Bis-(2-Chloroethyl) ether	45	80	80.0
	40		
	15		
Carbon Tetrachloride	14	13	20.4
	10		
	2		
Ethylenediamine	7	6	63.8
	10		
	0		
Isopropanol	0	0	N/A
	0		
	55		
N-Nitrosodimethylamine	84	73	21.7
	81		
	9		
Phenol	11	10	10.0
	10		
	32		
O-Xylene	29	31	5.0
	31		

Comparison of 20 MIL CPE Test Results and Potential Operational Requirements for LSCPE Users

In this section, the performance of 20 mil CPE, as measured by the tests conducted in this project, will be compared to a limited number of potential operational requirements that may confront the wearer of the LSCPE. The discussion in this section should not be taken as a firm recommendation for or against the use of 20 mil CPE in any specific situation. Determination of acceptability for specific situations should include the consideration by a qualified person of factors not addressed in the report, for example, temperature; probability of exposure; toxicity; type of exposure (immersion, splash, mist, vapor, etc.); surface area exposed; length of exposure; time available to escape, decontaminate, and doff the outer garment; other materials of construction of the garment.

As described in the introduction, the performance of 20 mil CPE was evaluated because this polymer comprises the primary outer garment material of a

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prototype ensemble undergoing advanced development in an EPA/Army project. The ensemble has a self-contained breathing supply with a duration of 2.5 hours; thus, at worst, the ensemble outer garment may be required to withstand 2.5 hours of chemical contact without degrading or becoming permeated.

With this 2.5 hour service life in mind, the performance of CPE was examined in two areas, one of which was *Permeation Breakthrough Resistance*. In this area, each CPE-chemical pair was placed in one of four categories based upon the breakthrough times observed in the permeation tests conducted in this project. The second performance area was *Tearing/Deformation Resistance*. In this area, each CPE-chemical pair was placed in one of two categories based upon the results obtained from the test in which CPE swatches were soaked in the test chemical and then repeatedly prodded with a blunt steel rod for up to two hours, as described in the procedures section.

Conclusions

The Long-term, Self-contained, Chemical Protective Ensemble (LSCPE), which has an outer garment constructed primarily of 20 mil CPE, has a self contained breathing air supply of 2.5 hours (150 minutes). Thus, to be fully satisfactory, the CPE must resist permeation by the test chemical for 150 minutes or more. Secondly, chemical contact should not seriously degrade the tearing resistance of the CPE after repeated prodding with a blunt steel rod.

- CPE (20 mil thick) demonstrated high resistance to both permeation and tearing when contacted by carbon tetrachloride and isopropanol. Four of the compounds that were tested, [isopropanol (> 480 min*), carbon tetrachloride (207 min*), phenol (175 min), and ethylenediamine (160 min)] had mean breakthrough times exceeding 150 minutes, and acetic acid (144 min) nearly met the 150 minute criterion. However, of the five compounds cited immediately above, only isopropanol and carbon tetrachloride did not degrade the ability of CPE to resist tearing after being subjected to repeated deformation. Phenol exposure caused serious loss of tearing resistance—each of three CPE samples stiffened and tore after repeated deformation. A less severe reduction in tearing resistance was caused following exposure to ethylenediamine and acetic acid.
- One compound, acetone, had a mean breakthrough time (15 min) that would pose problems for an LSCPE wearer, who would probably have to exit a contaminated work area and undergo decontamination before doffing the outer garmet.
- The mean permeation breakthrough times (42 to 87 minutes) for the remaining compounds [N-nitrosodimethylamine, o-xylene, acetic anhydride, and bis(2-chloroethyl) ether] indicate that moderate protection from permeation is provided. However, only acetic anhydride did not degrade the tearing resistance of CPE. N-nitrosodimethylamine, o-xylene, and bis(2-chloroethyl) ether caused each chemical-soaked CPE sample (three samples per chemical) to tear when subjected to repeated prodding with a blunt steel rod.

*Breakthrough times of <1 minute were also noted for isopropanol and carbon tetrachloride. Based on data for similar compounds and for the same compounds tested by different laboratories, it is likely that these very low breakthrough times are due to material imperfections or experimental error, although this has not been conclusively demonstrated.

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The complete report, entitled "Evaluation of the Resistance of a Chlorinated Polyethylene Protective Garment Material to Permeation and Degradation by Liquid Chemicals," (Order No. PB 85-242 337; Cost: $11.95, subject to change) will be available only from:

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